

Measuring the configurational temperature of a binary disc packing

Song-Chuan Zhao and Matthias Schröter*

Received Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

First published on the web Xth XXXXXXXXXX 200X

DOI: 10.1039/b000000x

Jammed packings of granular materials differ from systems normally described by statistical mechanics in that they are athermal. In recent years a statistical mechanics of static granular media has emerged where the thermodynamic temperature is replaced by a configurational temperature X which describes how the number of mechanically stable configurations depends on the volume. Four different methods have been suggested to measure X . Three of them are computed from properties of the Voronoi volume distribution, the fourth takes into account the contact number and the global volume fraction. This paper answers two questions using experimental binary disc packings: First we test if the four methods to measure compactivity provide identical results when applied to the same dataset. We find that only two of the methods agree quantitatively. Secondly, we test if X is indeed an intensive variable; this becomes true only for samples larger than roughly 200 particles. This result is shown to be due to recently found correlations between the particle volumes [Zhao *et al.*, *Europhys. Lett.*, 2012, **97**, 34004].

1 Is there a well defined configurational temperature?

Temperature is the concept that helps us to understand how the exchange of energy stored in the microscopic degrees of freedom follows from the accompanying change of entropy of the involved systems. If we coarse-grain our view to the macroscopic degrees of freedom of particulate systems, such as foams or granular gases, we can still define effective temperatures that describe their dynamics^{1,2}. This approach defines these systems as dissipative; kinetic energy of the particles is irrecoverably lost to microscopic degrees of freedom.

In the absence of permanent external driving such system will always evolve towards a complete rest. And in the presence of boundary forces or gravity this rest state will be characterized by permanent contacts between the particles which allow for a mechanical equilibrium. Shahinpoor³ and Kanatani⁴ were the first to suggest that such systems might still be amenable to a statistical mechanics treatment. Sam Edwards and coworkers^{5,6} have then developed this idea into a full statistical mechanics of static granular matter by using the ensemble of all mechanically stable states as a basis. A crucial requirement of such an approach is the existence of some type of excitation which lets the system explore the phase space of all allowed static configurations. This could e.g. be realized by tapping, cyclic shear, or flow pulses of the interstitial liquid. While there are promising results, the feasibility of this approach is still under debate⁷.

A second key concept in Edwards' approach is the replace-

ment of the energy phase space by a volume phase space where the volume function $W(\mathbf{q})$ takes the role of the classical Hamilton function. The configurations \mathbf{q} represent the positions and orientations of all grains. One can then define an analog to the partition function $Z(X)$:

$$Z(X) = \int e^{-W(\mathbf{q})/X} \Theta(\mathbf{q}) d\mathbf{q} \quad (1)$$

where $\Theta(\mathbf{q})$ limits the integral to mechanically stable configurations. X is the configurational temperature or compactivity, which is defined as $X = \partial V / \partial S$. The configurational entropy S corresponds to the logarithm of the number of mechanically stable configurations for a given set of boundary condition.

S is neither known from first principles (except for model systems^{8,9}) nor can it be measured directly. Therefore "thermometers" measuring X have to exploit other relationships; four different ways to do so have been suggested. In this paper we will test all four of them using the same dataset of mechanically stable disc packings.

First X can be determined from the steady state volume fluctuations using an analog to the relationship between specific heat and energy fluctuations^{10–13}; we will refer to this compactivity as X_{VF} . A second method is based on the probability ratio of overlapping volume histograms^{14,15}, allowing us to compute X_{OH} . A third way^{16,17} computes X_{Γ} from Gamma function fits to the volume distribution. Finally, it has been suggested very recently¹⁸, that an analysis based on "quadrons"¹⁹ instead of Voronoi cells leads to an expression for X_Q that involves the average particle volume and the contact number.

This difference in approach immediately raises the question if these four methods provide identical results when applied

Max Planck Institute for Dynamics and Self-Organization (MPIDS), 37077 Goettingen, Germany

* matthias.schroeter@ds.mpg.de

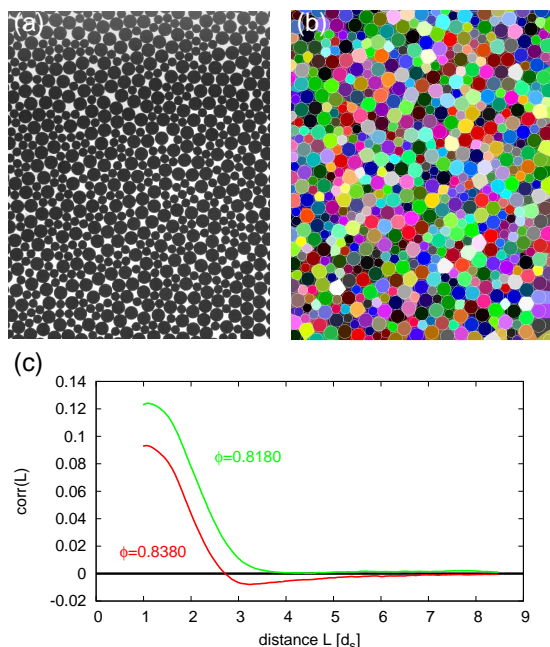


Fig. 1 Correlations in binary disc packings. a) experimental image and b) the corresponding Voronoi tessellation. c) The correlation between two Voronoi volumes as a function of their distance L (measured in units of small disc diameters d_s). Dense packings exhibit anti-correlations for L larger than approx. $2.5 d_s$. Reproduced from²³.

to the same experiment. There have been two previous experiments addressing this question: McNamara *et al.*¹⁵ found that X_{VF} and X_{OH} agree for tapped packings of approximately 2000 glass spheres. The same result has been reported by Puckett and Daniels²⁰ for compressed disc packings.

The full description of a granular packing has to take the boundary stresses into account^{18,21}. The stress dependence of the entropy then gives rise to a tensorial temperature named angoricity. Angoricity has been computed from numerics using the overlapping histogram method²² and from experiments using both fluctuations and overlapping histograms²⁰. As the experiments described below are performed in an open cell with gentle driving, the boundary stresses can be assumed to be small and constant; we therefore exclude angoricity from our further analysis.

2 Correlations in the Voronoi-volume of disc packings

The three methods to compute X_{VF} , X_{OH} , and X_Γ all start from the Voronoi-volume distribution. However, it has been shown that the Voronoi volumes inside a sample are corre-

lated²⁴. We recently measured the spatial extension of this correlations and demonstrated the existence of additional anti-correlations between the volumes²³. These correlations raise the question if X is indeed an intensive parameter i.e. if its value is independent of the number N of particles analyzed? As the Voronoi-volumes reported in reference²³ will be the basis of this study we quickly recap the relevant experimental procedures and results, more details can be found in the original publication.

2.1 Experimental setup

The experiment is performed in an air-fluidized bed filled with a binary mixture of Teflon discs with $d_s = 6\text{mm}$ and $d_l = 9\text{mm}$ diameter. Data sets of 8000 different mechanically stable configurations are prepared by repeated air pulses. Changing pressure and duration of the air pulses allows us to control the average packing fractions ϕ in the ranges of 0.818 to 0.838. After each flow pulse the discs come to a complete rest and are then imaged with a CCD camera (Fig. 1 a). After detecting the particle centers, the Voronoi volume V of each disc is determined (Fig. 1 b). We then compute the free volume $v_f = V - V_{min}$ for each particle with v_{min} being the volume the grain would occupy in a hexagonal packing of identical discs. This step allows us to superimpose the results for small and large discs in the subsequent analysis.

Our results will also depend on the packing fraction of the loosest possible packing $\phi_{RLP} = 0.811$. This value is averaged over 10 packings prepared by slowly settling the discs in a manually decreased air flow.

2.2 Correlations in binary disc packings

The correlation between the Voronoi volumes can be measured using:

$$corr(L) = \frac{\langle (v_{f,i} - \bar{v}_{f,i})(v_{f,j} - \bar{v}_{f,j}) \rangle}{\sigma_f^2} \quad (2)$$

Here i, j are two points in the packing which separated by a distance L . The free volumes at these points are $v_{f,i}$ and $v_{f,j}$; $\langle \dots \rangle$ indicates averages over all 8000 different packings and 240 pairs of points i, j within each packing. σ_f^2 is the variance of the free volumes averaged over the two points.

Figure 1 c) depicts $corr(L)$ for two different packing fractions. At low values of ϕ only positive correlation between Voronoi cells are found. Above $\phi_{AC} = 0.8277$ anti-correlations appear for L larger than approximately 2.5 small particle diameters. We will show below that these (anti-) correlations control how X becomes intensive.

3 Compactivity X_{VF} measured from volume fluctuations

This methods starts from the assumption of a Boltzmann like probability distribution:

$$p(\mathbf{q}, X) = \frac{e^{-W(\mathbf{q})/X}}{Z(X)} \Theta(\mathbf{q}) \quad (3)$$

From equation 3 follows for the probability to observe a certain volume V at a given compactivity X :

$$\begin{aligned} p(V, X) &= \int \delta(W(\mathbf{q}) - V) p(\mathbf{q}, X) d\mathbf{q} \\ &= \mathcal{D}(V) \frac{e^{-V/X}}{Z(X)} \end{aligned} \quad (4)$$

where the density of states $\mathcal{D}(V) = \int \delta(W(\mathbf{q}) - V) \Theta(\mathbf{q}) d\mathbf{q}$ counts the number of the mechanical stable states available at volume V . Using equation 4 we can determine the average volume $\bar{V}(X)$ as

$$\bar{V}(X) = \int \mathcal{D}(V) \frac{e^{-V/X}}{Z(X)} V dV \quad (5)$$

Taking the derivative of eq. 5 with respect to $1/X$ shows that

$$\frac{\partial \bar{V}}{\partial(1/X)} = -(V - \bar{V})^2 = -\sigma_V^2 \quad (6)$$

on the other hand $\partial \bar{V} / \partial(1/X)$ can be rewritten as $-X^2 \partial \bar{V} / \partial X$ from which follows:

$$X^2 \frac{d\bar{V}}{dX} = \sigma_V^2 \quad (7)$$

Nowak *et al.* were the first to suggest that integrating eq. 7 provides a way to compute X^{10} :

$$\frac{1}{X_{VF}} = \int_{\bar{V}}^{\bar{V}_{RLP}} \frac{d\bar{V}}{\sigma_V^2} \quad (8)$$

where the compactivity at the loosest possible packing has been set to infinity: $X|_{RLP} = \infty$. First measurements^{11,12} of X_{VF} showed that it indeed measures a material property as it depends on the roughness of the particles. It has to be pointed out that this method has the epistemological status of a calculation rule and not of a test of the Boltzmann assumption made in eq. 3. This is different for the overlapping histogram method described below.

As described in section 2 we are interested in the evolution of X with the size of the analyzed region, in the following referred to as cluster. Therefore we continue our study by using the normalized average volume per particle $v = 1/N \sum V/V_g$ where the sum goes over all N particles inside the cluster, V is the Voronoi volume of the individual particles and V_g the volume occupied by the particle itself. As a consequence of this choice also X is dimensionless.

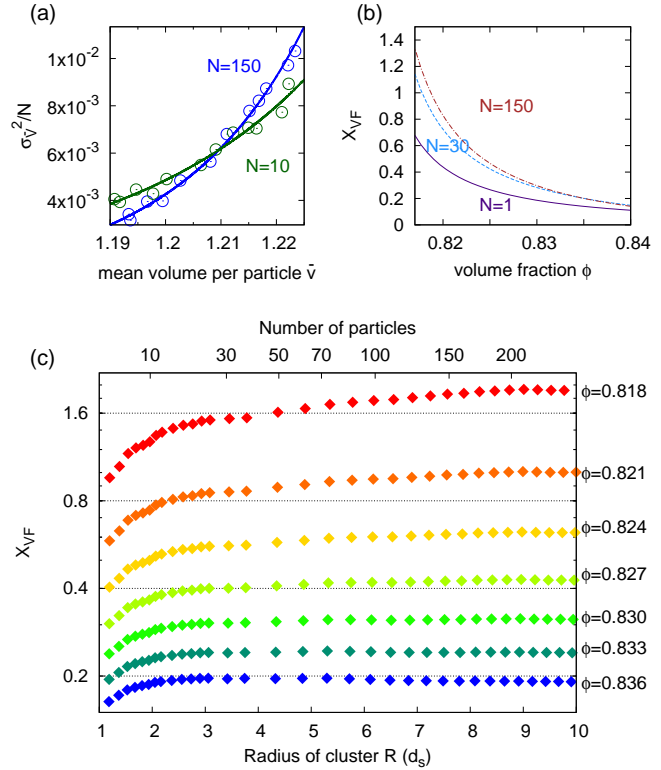


Fig. 2 Compactivity X_{VF} measured from volume fluctuations. a): Average volume variance σ_v^2 versus average volume \bar{v} measured for clusters of size $N = 10, 150$. The solid curves are power law fits which are then used to numerically integrate eq. 8. (b): The compactivity X_{VF} computed from eq. 8 for three different cluster sizes. (c): The evolution of X_{VF} with cluster sizes at different values of ϕ . The radius R of the analyzed cluster is proportional to $\sqrt{N/\phi}$.

3.1 Experimental results

Figure 2 (a) shows that for our tapped disc packings the variance of the volume fluctuation σ_v^2 increases monotonically with the average volume \bar{v} (bar meaning the average over all 8000 taps). To compute X_{VF} we perform a power law fit to σ_v^2 and use the result to integrate equation 8 numerically. Figure 2 (b) shows how the resulting X_{VF} depends on the packing fraction at cluster sizes N of 1, 30, and 150 discs. It is obvious that is not an intensive variable at this range of N .

3.2 Correlations make X_{VF} non-intensive in small systems

For a more detailed analysis we have plotted in figure fig. 2(c) the dependence of X_{VF} on the cluster radius R measured in small disc diameters d_s . Three features of X_{VF} become apparent:

1. X_{VF} is growing monotonously for $R < 3d_s$ for all val-

ues of ϕ ,

- for low to intermediate values of ϕ , X_{VF} then reaches a plateau, and
- for the highest packing fraction X_{VF} first decreases slightly before entering a plateau.

All three points can be understood by considering the influence of the volume correlations shown in figure 1. Equation 8 computes X_{VF} from the average variance σ_v^2 inside the cluster. This variance can be decomposed in the following way:

$$\begin{aligned}\sigma_v^2 &= \frac{1}{N} \sum_k \sum_m \langle \delta v_k \delta v_m \rangle \\ &= \frac{1}{N} \sum_k (\sigma_k^2 + \sum_{m \neq k} \langle \delta v_k \delta v_m \rangle)\end{aligned}\quad (9)$$

Here $\sigma_k^2 = \langle \delta v_k^2 \rangle$ is the fluctuation of a single Voronoi cell and $\sum_{m \neq k} \langle \delta v_k \delta v_m \rangle := I_k$ is the volume correlation between disc k and all other discs inside the cluster. If k is in the center of the cluster, then I_k is proportional to the area enclosed by $\text{corr}(L)$, the zero line, and $L = R$ in figure 1(c).

This consideration allows us to explain feature 1: while N goes from 2 to approximately 25 all I_k are positive and growing. Consequentially, the variance of the cluster σ_v^2 is larger than the sum of the variance of the individual Voronoi cells $1/N \sum \sigma_k^2$ and X_{VF} grows monotonously with N .

The second feature stems from the fact, that once disk k is more than four to five d_s away from the boundary of the cluster, I_k becomes independent of the cluster size. As the relative importance of "boundary discs" decreases with cluster size, σ_v^2 goes to a constant and X_{VF} becomes independent of N .

Finally, the slight decrease in X_{VF} at high packing fractions and N values between approximately 30 and 150 can be attributed to the anti-correlations that appear for ϕ larger than 0.8277; these will decrease I_k slightly again before it reaches its plateau value.

4 Compactivity X_{OH} measured from overlapping histograms

This way to compute compactivity has been first described by Dean and Lefèvre¹⁴. It uses pairs of experiments with slightly different values of ϕ respectively X_{OH} and computes then the ratio of the probabilities to observe the same local volume V . If the assumption of a Boltzmann-like probability distribution, as expressed in equation 4, holds, this ratio should be exponen-

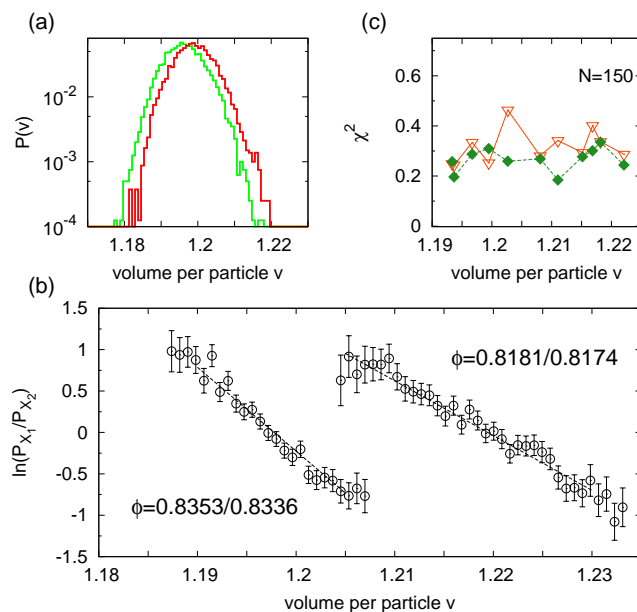


Fig. 3 Compactivity measured with the overlapping histogram method. (a) The probability to observe an average volume per particle in clusters with 150 disks. The average packing fraction corresponds to 0.8336 for the red curve, and 0.8353 for the green curve. (b) The logarithm of the probabilities to observe a given volume at two different compactivities respectively packing fractions is a linear function of the volume, which is in accordance with eq. 11. Cluster size is 150 discs, the dashed lines are linear fits. (c) The χ^2 values provide a goodness of fit test for both linear (green diamonds) and parabolic (red triangle) fits to the probability ratios shown in panel b). The average χ^2 is 13% smaller for the linear fit, indicating that a Boltzmann-like distribution is a better assumption than a Gaussian.

tial in V :

$$\frac{p(V, X_1)}{p(V, X_2)} = \frac{\frac{\mathcal{D}(V)e^{-V/X_1}}{Z(X_1)}}{\frac{\mathcal{D}(V)e^{-V/X_2}}{Z(X_2)}} = \frac{Z(X_2)}{Z(X_1)} e^{-(\frac{1}{X_1} - \frac{1}{X_2})V} \quad (10)$$

By taking the logarithm on both sides we obtain:

$$Q := \ln \frac{p_{X_1}(V)}{p_{X_2}(V)} = \left(\frac{1}{X_2} - \frac{1}{X_1} \right) V + \ln \frac{Z_{X_2}}{Z_{X_1}} \quad (11)$$

Therefore the difference between two compactivities can be computed from a line fit of Q versus V as it was first demonstrated in¹⁵.

Figure 3(a) shows the distribution of average volumes for two experiments with a packing fraction difference of 0.0017. Figure 3(b) demonstrates that the ratio Q is indeed a linear function of V , as predicted by eq. 11. By sweeping the experimentally accessible range of packing fractions, X_{OH} can be determined from the accumulated compactivity differences up to an additive constant X_0 . We determine X_0 by setting X_{OH}

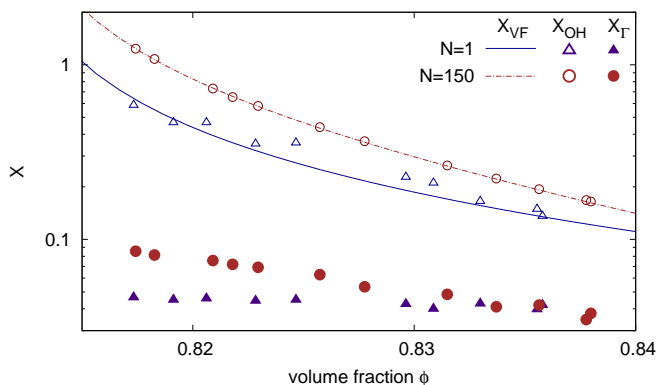


Fig. 4 Comparison of X_{OH} , X_{VF} , and X_{Γ} computed for single discs and clusters of 150 particles. In all three cases the compactivity of an individual particle is smaller than that of a larger cluster. X_{OH} and X_{VF} agree quantitatively, X_{Γ} is about an order of magnitude smaller.

for the loosest experimental packing to the value of X_{VF} at this volume fraction.

The resulting X_{OH} is shown in figure 4. The good quantitative agreement of X_{OH} and X_{VF} is not too surprising given that a) both methods are derived from the same probability distribution (eq. 4) and b) our determination of X_0 . However, the X_{OH} method provides an additional test of assumption 4 as we can compare the quality of a linear fit to $Q(V)$ with fit functions derived from alternative probability distribution functions¹⁵. A generic candidate would be a Gaussian distribution which results in parabolic fit. Figure 3(c) demonstrates however that a linear fit is superior, adding credibility to a Boltzmann-like approach. Also note that canceling the density of states in equation 10 implicitly assumes a weak form of ergodicity; if the system explores its phase space different at the two values of X we can't eliminate $\mathcal{D}(V)$.

5 Compactivity X_{Γ} measured from a Gamma distribution fit

This third method to compute compactivity has been suggested by Aste and Di Matteo^{17,25}; it differs from the previous approaches that it explicitly determines the density of states $\mathcal{D}(V)$. Based on the observation¹⁶ that experimental Voronoi volume distributions can be well fit by Γ distributions, the propose to replace equation 4 with a rescaled k -Gamma distribution

$$p(V_f) = \left(\frac{k}{\bar{V}_f}\right)^k \frac{V_f^{(k-1)}}{\Gamma(k)} \exp\left(-k \frac{V_f}{\bar{V}_f}\right) \quad (12)$$

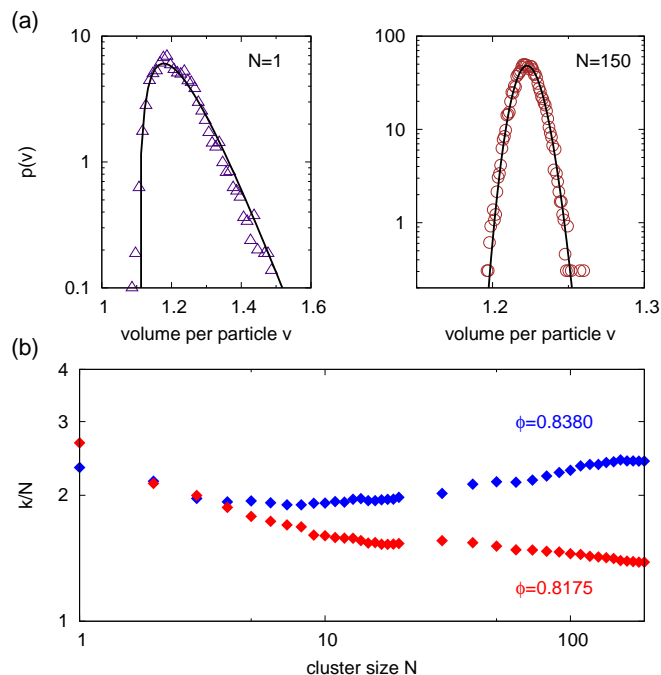


Fig. 5 Applying the Γ distribution method. (a) Γ distribution fits to the volume distributions for a single discs and a 150 particle clusters ($\phi = 0.8175$). (b) Evolution of the normalized shape factor with cluster size.

where \bar{V}_f is the mean free volume (as defined in section 2), and k is the shape factor. They then identify

$$X_{\Gamma} = \frac{\bar{V}_f}{k} \quad (13)$$

or by making use of the fact that variance $\sigma_{\bar{V}_f}^2$ of the Γ function is given by: $\sigma_{\bar{V}_f}^2 = \bar{V}_f^2/k$ they derive

$$X_{\Gamma} = \frac{\sigma_{\bar{V}_f}^2}{\bar{V}_f} \quad (14)$$

By comparing equation 4 and equation 12 we can also identify the density of states:

$$\frac{\mathcal{D}(V)}{Z(X)} = X_{\Gamma}^{-k} \frac{V_f^{(k-1)}}{\Gamma(k)} \quad (15)$$

Figure 5 (a) demonstrates that our volume distribution is well fit by a Γ distribution. We then determine X_{Γ} without any additive constant using equation 14. Figure 4 show X_{Γ} in comparison to X_{VF} and X_{OH} . While there are qualitative similarities as monotonous decrease with ϕ and the increase with N , both the absolute values and the slope of X_{Γ} is quite different from the other two methods.

The increase of X_Γ with cluster size points again to the influence of the volume correlations. In figure 5 (b) the normalized shape factor k/N is plotted as a function of N . Similar to the evolution of X_{VF} in figure 2 (c), X_Γ will monotonously increase towards a plateau for small values of ϕ and go through a maximum before the plateau for the densest packings.

6 Compactness X_Q measured from quadron tessellation

In a very recent paper Blumenfeld *et al.*¹⁸ have presented an analysis of the statistical mechanics of two-dimensional packings based on a quadrons¹⁹ as the building blocks of the tessellation. An advantage of this choice is that the quadrons take by design into account the structural degrees of freedom of the individual particles. They then write down the partition functions of the volume ensemble Z_V , the force ensemble Z_F , and the total partition function Z , showing in this process that $Z \neq Z_V Z_F$. Finally, they derive from Z an expression for X_Q of an isostatic packing:

$$X_Q = \frac{2}{\bar{z}N + M} \bar{V} \quad (16)$$

\bar{V} is the average volume per particle, \bar{z} the average number of contact a particle has, and M is the number of boundary forces.

If X_Q is derived from Z_V instead of Z one obtains:

$$X_Q = \frac{2}{\bar{z}N} \bar{V} \quad (17)$$

In comparing our results with this approach we have to acknowledge a number of differences. Our experimental packings are clearly subject to volume forces due to gravity and they are also, as shown in figure 6 (a), hyperstatic. I.e. their contact number is larger than what is required to fix all their mechanical degrees of freedom.

Generally, frictional particles only become isostatic at Random Loose Packing and zero pressure²⁶. Therefore the only direct comparison possible is at our RLP value $\phi = 0.811$, the corresponding X_Q is shown as black circle in figure 6 (c). If we assume that we can replace \bar{z} in equation 16 with $\bar{z}(\phi)$ and use the contact numbers displayed in figure 6 (a), we can also compute X_Q for a larger range of ϕ . These results are indicated as the open squares in figure 6 (c).

As X_Q is only computed from the average volume per particle, it is insensitive to the correlations described in section 2. On the other hand there exists a finite size effect if X_Q is only computed from the volume ensemble, ignoring the boundary forces. Figure 6 (b) shows how the differences between X_Q computed from the full and the volume ensemble

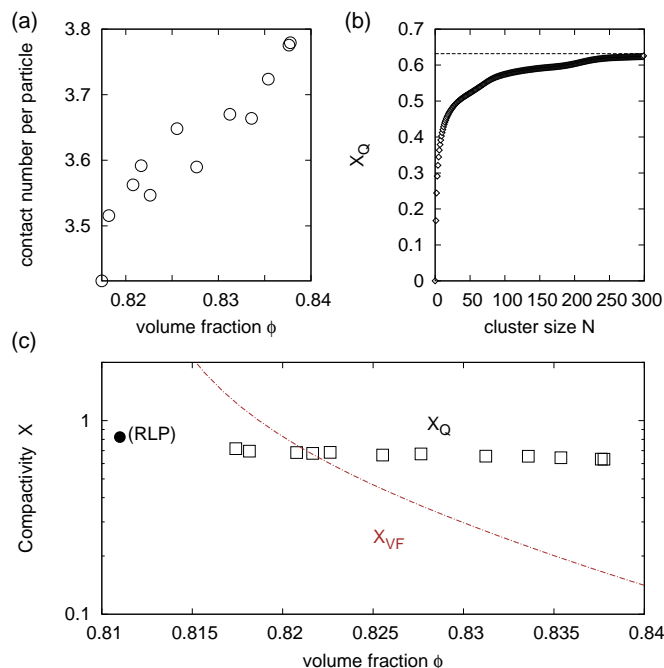


Fig. 6 Compactness measured with the quadron tessellation method. (a) In all our experiments the contact number per particle is above the isostatic value of 3. (b) A comparison of X_Q computed from the full partition function (eq. 16, dashed line) and X_Q derived from only the volume ensemble (eq. 17, circles). (c) A comparison of X_{VF} measured for $N = 150$ and X_Q . The filled circle is computed for our Random Loose Packing value which is presumably the only isostatic point in our dataset. The open squares assume that equation 16 is also valid for hyperstatic packings.

vanishes with increasing cluster size and consequentially decreasing contribution of M .

We acknowledge helpful discussions with Karen Daniels and Klaus Kassner.

References

1. I. K. Ono, C. S. O'Hern, D. J. Durian, S. A. Langer, A. J. Liu and S. R. Nagel, *Phys. Rev. Lett.*, 2002, **89**, 095703.
2. N. V. Brilliantov and T. Pöschel, *Kinetic Theory of Granular Gases*, Oxford University Press, 2004.
3. M. Shahinpoor, *Powder Technology*, 1980, **25**, 163–176.
4. K.-I. Kanatani, *Powder Technology*, 1981, **30**, 217–223.
5. S. Edwards and R. Oakeshott, *Physica A*, 1989, **157**, 1080–1090.
6. A. Mehta and S. F. Edwards, *Physica A*, 1989, **157**, 1091–1100.
7. M. Pica Ciamarra, P. Richard, M. Schröter and B. P. Tighe, *Soft Matter*, 2012, **8**, 9731.
8. R. Monasson and O. Pouliquen, *Physica A*, 1997, **236**, 395–410.
9. R. K. Bowles and S. S. Ashwin, *Physical Review E*, 2011, **83**, 031302.
10. E. R. Nowak, J. B. Knight, E. Ben-Naim, H. M. Jaeger and S. R. Nagel, *Phys. Rev. E*, 1998, **57**, 1971–1982.

-
- 11 M. Schröter, D. I. Goldman and H. L. Swinney, *Phys. Rev. E*, 2005, **71**, 030301.
 - 12 P. Ribière, P. Richard, P. Philippe, D. Bideau and R. Delannay, *Europ. Phys. J. E*, 2007, **22**, 249 – 253.
 - 13 C. Briscoe, C. Song, P. Wang and H. A. Makse, *Physical Review Letters*, 2008, **101**, 188001–4.
 - 14 D. S. Dean and A. Lefvre, *Phys. Rev. Lett.*, 2003, **90**, 198301.
 - 15 S. McNamara, P. Richard, S. K. de Richter, G. Le Car and R. Delannay, *Phys. Rev. E*, 2009, **80**, 031301.
 - 16 T. Aste, T. D. Matteo, M. Saadatfar, T. J. Senden, M. Schröter and H. L. Swinney, *EPL*, 2007, **79**, 24003.
 - 17 T. Aste and T. Di Matteo, *Phys. Rev. E*, 2008, **77**, 021309.
 - 18 R. Blumenfeld, J. F. Jordan and S. F. Edwards, *Physical Review Letters*, 2012, **109**, 238001.
 - 19 R. Blumenfeld and S. F. Edwards, *Physical Review Letters*, 2003, **90**, 114303.
 - 20 J. G. Puckett and K. E. Daniels, *Physical Review Letters*, 2013, **110**, 058001.
 - 21 L. A. Pugnali, J. Damas, I. Zuriguel and D. Maza, *Papers in Physics*, 2011, **3**, 030004.
 - 22 S. Henkes, C. S. O'Hern and B. Chakraborty, *Physical Review Letters*, 2007, **99**, 038002–4.
 - 23 S. Zhao, S. Sidle, H. L. Swinney and M. Schröter, *EPL*, 2012, **97**, 34004.
 - 24 F. Lechenault, F. d. Cruz, O. Dauchot and E. Bertin, *J. Stat. Mech.*, 2006, **2006**, P07009–P07009.
 - 25 T. Aste and T. Di Matteo, *The European Physical Journal B*, 2008, **64**, 511–517.
 - 26 K. Shundyak, M. van Hecke and W. van Saarloos, *Phys. Rev. E*, 2007, **75**, 010301(R).
 - 27 F. Lechenault and K. E. Daniels, *Soft Matter*, 2010, **6**, 3074.
 - 28 E. T. Jaynes, *Physical Review*, 1957, **106**, 620–630.
 - 29 V. Senthil Kumar and V. Kumaran, *The Journal of Chemical Physics*, 2005, **123**, 114501–114501–13.